

Novel phosphorus-modified polysulfone as a combined flame retardant and toughness modifier for epoxy resins

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Received 26 September 2006; accepted 4 December 2006

Available online 8 January 2007

Abstract

A novel phosphorus-modified polysulfone (P-PSu) was employed as a combined toughness modifier and a source of flame retardancy for a DGEBA/DDS thermosetting system. In comparison to the results of a commercially available polysulfone (PSu), commonly used as a toughness modifier, the chemorheological changes during curing measured by means of temperature-modulated DSC revealed an earlier occurrence of mobility restrictions in the P-PSu-modified epoxy. A higher viscosity and secondary epoxy-modifier reactions induced a sooner vitrification of the reacting mixture; effects that effectively prevented any phase separation and morphology development in the resulting material during cure. Thus, only about a 20% increase in fracture toughness was observed in the epoxy modified with 20 wt.% of P-PSu, cured under standard conditions at 180 °C for 2 h. Blends of the phosphorus-modified and the standard polysulfone (PSu) were also prepared in various mixing ratios and were used to modify the same thermosetting system. Again, no evidence for phase separation of the P-PSu was found in the epoxy modified with the P-PSu/PSu blends cured under the selected experimental conditions. The particular microstructures formed upon curing these novel materials are attributed to a separation of PSu from a miscible P-PSu–epoxy mixture. Nevertheless, the blends of P-PSu/PSu were found to be effective toughness/flame retardancy enhancers owing to the simultaneous microstructure development and polymer interpenetration.

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Keywords: Flame retardants; Phosphorus-modified polysulfone; Fracture toughness

1. Introduction

Epoxy resins are widely used as high-performance matrices in fibre-reinforced composites for many modern engineering applications. As a result of the increasing usage of such polymers, varying qualification requirements as well as the current trend towards the sustainable conservation of resources, the flame resistance and thermal stability as well as the toxicological consequences of combustion of flame-retarded epoxies

have recently become a subject of considerable attention [1]. Many approaches have been made to improve the fire–smoke-toxicity (FST) properties of epoxy resins using either non-reactive or reactive flame retardants [1–8]. However, as many cured epoxies are already rather brittle in nature due to their high crosslinking density, the addition of such flame retardants often induces a further severe degradation of the overall physical and mechanical properties of the resulting material [9–11]. Traditional concepts to overcome the problem of epoxy brittleness are: (i) the addition of liquid rubber copolymers with various functional end groups [12–16] and (ii) a modification based on thermoplastics [17–30]. Yet, a combined addition of both modern flame retardants and

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established toughness modifiers in order to optimise the overall product performance has not been extensively studied so far.

Although the addition of liquid rubbers in general has been successfully proven to lead to a high fracture toughness of the epoxy, such liquid rubbers often induce a severe degradation of other key properties of the system such as the hot/wet behaviour, the elastic modulus, and the glass transition temperature [15,31,32]. In addition, owing to the low thermal stability of the rubber, the decreasing thermal stability of the final material also is a disadvantage. In contrast, thermoset-toughening using thermoplastics often provides an effective means to minimise or even avoid this pronounced loss in stiffness, glass transition temperature, and thermal stability of the thermoset material.

Many studies have been devoted to the evaluation of high-temperature thermoplastics such as poly(ethersulfone)s (PES) [14,19,29,33–35], poly(sulfone)s (PSu) [17,20–22,26–28,30] or poly(etherimide)s (PEI) [36–39] as toughening modifiers. In the case of an epoxy–amine system for example, a homogeneous blend is initially obtained when using suitable thermoplastics. With the advancement of the curing reaction the molecular weight of the epoxy–amine network increases and, consequently, the solubility of the thermoplastic in the mixture decreases and two phases are formed as a result of a reduction in the entropic contribution to the free energy of mixing during polymerisation [40,41]. It is this phase separation that leads to the desired improvement in fracture toughness of the epoxy without the deterioration of other mechanical properties. However, the fracture toughness enhancement strongly correlates with the final morphology of the two-phase system; a co-continuous or phase-inverted morphology especially is necessary in order to achieve a significantly higher fracture toughness of the material [19,26,27,31,42–44]. As commonly used flame retardants often lead to a significantly altered curing behaviour of epoxies, the combined addition of such flame retardants and toughness modifiers might not lead to the required morphology evolution in a straight-forward manner.

Somewhat surprising, little attempts have been made so far to combine both desirable functions in a single compound – to increase the flame retardancy and at the same time to improve the mechanical properties of epoxy systems by the addition of phosphorus-modified thermoplastics. An initial study [45] showed the feasibility of introducing phosphorus-containing groups into the chemical backbone of suitable thermoplastics, leading to the successful synthesis of a novel halogen-free flame retardant poly(sulfone) (P-PSu) with a glass transition temperature (T_g) exceeding 200 °C and of a poly(ether ether ketone) (P-PEEK) with an improved thermal stability. The incorporation of these novel modifiers into an amine-cured DGEBA epoxy system showed some promising improvements in flame retardancy as determined by the limiting oxygen index (LOI) [45,46], although no significant enhancement of the fracture toughness could be detected in these preliminary studies.

In order to further evaluate the potential of such phosphorus-modified poly(sulfone) (P-PSu) as a flame retardant and

toughness modifier, a detailed characterisation of the curing kinetics and solid-state properties of a difunctional bisphenol-A based epoxy resin cured with an aminic hardener as a function of the weight fraction of the modified thermoplastic was carried out. Experimental results regarding the curing behaviour and phase separation are compared to a reference system based on a commercial PSu toughness modifier. As demonstrated here, the morphology evolution of the modified epoxy under various processing conditions reflects the chemical structure of the additive, which, in turn, influences the resulting fracture mechanical properties as well as the fire behaviour and flammability of the system. Lastly, promising results regarding the combined addition of both the modified and the commercial reference thermoplastic are presented, an approach that effectively allows the tailoring of the final product performance.

2. Experimental

2.1. Materials

A difunctional epoxy resin (DGEBA, Ruetapox 0162) with an epoxy equivalent weight of 173 g/eq and free of hydroxyl groups was supplied by Bakelite and was used as received. The 4,4'-DDS hardener, with an amine equivalent weight of 62 g/eq (synthesis grade), was purchased from Merck and was also used as received. The thermoplastic modifiers were a novel phosphorus-containing polysulfone (P-PSu), designed and synthesised in our laboratory ($M_w = 32.900 \text{ g mol}^{-1}$, $M_n = 9200 \text{ g mol}^{-1}$, $T_g = 228 \text{ °C}$) [45] and a commercial grade polysulfone (PSu, Ultrason-S2010, BASF AG; $M_w = 41.800 \text{ g mol}^{-1}$, $M_n = 13.400 \text{ g mol}^{-1}$, $T_g = 185 \text{ °C}$). The chemical structures of the materials used in this study are summarised in Fig. 1.

2.2. Preparation and curing procedure of thermoplastic-modified epoxy

Initially, epoxy formulations containing 0, 5, 10, 15, and 20 wt.% of the commercial PSu reference and of the phosphorus-modified P-PSu were prepared. In the case of the P-PSu, the selected weight fractions of the thermoplastic correspond to phosphorus contents of 0.3, 0.6, 0.9, and 1.2 wt.%. All formulations were prepared according to the following identical experimental procedure. The DGEBA was placed in a glass flask and was heated to 130 °C in an oil bath connected to a temperature controller. The desired amount of either type of polysulfones as fine powder (particle size < 8 µm) was then added slowly to the epoxy resin at this temperature and was extensively mixed using a mechanical stirrer until it was completely dissolved and the mixture was again homogeneous. Blends of P-PSu and PSu at different ratios (25:75, 50:50 and 75:25) were also mixed with the DGEBA, keeping the total amount of modifier in the mixture constant at 20 wt.% in order to maximise the phosphorus content in the system. Maintaining the temperature at 130 °C, the DDS was then incorporated into the mixture keeping a DGEBA/DDS mixing

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